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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Synthetic Zeolite Production

We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Finsbury Circus, London, E.C.2, a company incorporated in accordance with the Laws of England, and PAUL ANTHONY LAWRENCE and ROBERT WILLIAM AITKEN, both of BP Research Centre, Chertsey Road, Sunbury on Thames, Middlesex, both of British nationality, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to the production of synthetic zeolites from montmorillonite clays.

According to the present invention synthetic zeolites are prepared by acid treating a montmorillonite clay, neutralising the mix, washing with water, and heating the residue under reflux with a solution containing sodium hydroxide and a silica sol.

The acid treatment is preferably carried out under reflux with a strong mineral acid e.g. sulphuric acid or hydrochloric acid in a concentration of 1%-40% by weight and a clay to acid weight ratio between 0.1 and 4.0 for $\frac{1}{2}$ to 24 hours at reflux temperature. Neutralisation is preferably carried out using ammonia and the water washing is conducted with distilled water until the residue is substantially salt-free.

The residue is preferably suspended in a solution containing between 15 and 35% wt NaOH and to this is added a silica sol containing 30% wt SiO_2 . Between 700 g and 900 g of sodium hydroxide solution per 100 g of clay is used together with between 700 g and 900 g of silica sol per 100 g clay. The mix is refluxed until crystallisation is substantially complete, i.e. about 60 hours.

It has been found that by using the procedure given above a mixture of zeolites can be obtained containing a high proportion of faujasite and zeolites in the chabazite-gmelinite

nite series. The zeolite product obtained according to the present invention is useful as a catalyst or catalyst support material. In particular, the incorporation of Group VIII metals, particularly metals of the platinum group, on the zeolite obtained according to the present invention gives active cracking and hydrocracking catalysts.

The invention is illustrated by the following examples:—

EXAMPLE 1

A montmorillonite from Chambers, Arizona was refluxed for 20 hours with 25% sulphuric acid using a clay to acid ratio of 1:1. The acid was then neutralised using ammonia, and the mix filtered. The filtrate was washed with distilled water until sulphate free.

25 g of the acid treated clay was mixed with 200 g of water, and 48 g of NaOH and 200 g of a silica sol containing 30% SiO_2 was added. The mixture was refluxed in a boiling water bath for 65 hours. The residue was filtered off and washed to a pH of about 10.

A sample of the residue was examined by X-ray diffraction and found to be substantially entirely zeolite, the main constituent being faujasite but with an appreciable amount of a zeolite in the chabazite gmelinite series.

EXAMPLE 2

The process of Example 1 was repeated using a montmorillonite from Upton, Wyoming.

The product obtained was again found to be substantially entirely zeolite, the main constituents being a member of the chabazite-gmelinite series but with an appreciable amount of faujasite present.

In both examples the cell parameter of the faujasite produced was in the range 24.6-24.8Å.

EXAMPLE 3

100 g of the zeolite prepared in Example 1 was ammonium exchanged by refluxing four times for four hours each time with an ammonium chloride solution. A fresh solution was used for each exchange. This solution contained 74 g of ammonium chloride and 400 g of water. The zeolite was filtered after each exchange and after the final exchange it was washed until chloride free. The zeolite was then dried at 120°C.

The ammonium exchanged zeolite was palladium exchanged using tetrammine palladium chloride. The zeolite was suspended in 135

ml of water and to it was added a solution of 0.8 g of tetrammine palladium chloride in 135 ml of water. This solution was added dropwise over about 3 to 4 hours and stirring was continued for a further 16 hours. The zeolite was then filtered and washed until chloride free. It was then dried, pelleted to $\frac{1}{8}$ inch and granulated to 8-16 mesh BSS. It was finally calcined in a flow of air for 2 hours at 500°C.

The catalyst prepared as described above was tested in an atmospheric pressure micro-reactor using n-heptane feedstock, under the following conditions:—

Pressure : atmospheric

Hydrogen to hydrocarbon mole ratio : 7.4:1

Space velocity : 480 volumes of gas/volume of catalyst /hour

In the table given below the conversion of n-heptane at different temperatures are compared with those obtained with palladium on a commercial silica-alumina catalyst. The

commercial cracking catalyst was ammonium exchanged and palladium exchanged in the same way as the zeolite based catalyst.

Catalyst		Catalyst Temperature °C		
		250	300	350
Pd on zeolite (zeolite made from montmorillonite clay)	Conversion of n-heptane % mole	25.7	85.1	99.3
Pd on commercial silica-alumina cracking catalyst	Conversion of n-heptane % mole	5.1	24.6	79.2

These results show that palladium on zeolite made from montmorillonite is a very active catalyst.

WHAT WE CLAIM IS:

1. A method of preparing synthetic zeolites comprising acid treating a montmorillonite clay, neutralising the mix, washing with water, and heating the residue under reflux with a solution containing sodium hydroxide and a silica sol.

2. A method as claimed in claim 1 wherein the acid treatment is carried out under reflux with sulphuric acid or hydrochloric acid in a concentration of 1-40% by weight and a clay to acid weight ratio between 0.1 and 4.0 for $\frac{1}{2}$ -24 hours at reflux temperature.

3. A method as claimed in claim 1 or claim 2 wherein the neutralisation is carried out using ammonia and the water washing is conducted with distilled water until the residue

is substantially salt-free.

4. A method as claimed in any of claims 1-3 wherein the residue is suspended in a solution containing 15-35% by weight of NaOH to which is added a silica sol containing 30% by weight SiO_2 , between 700 g and 900 g of NaOH solution per 100 g of clay and between 700 g and 900 g of silica sol per 100 g of clay being used, refluxing being continued until crystallisation is substantially complete.

5. Synthetic zeolites prepared according to any of claims 1-4.

6. A process for cracking hydrocarbons wherein synthetic zeolites as claimed in claim 5 are used as catalyst or catalyst support material.

7. A process for hydrocracking hydrocarbons wherein synthetic zeolites as claimed in claim 5 are used as catalyst or catalyst support material.

8. A method as claimed in claim 1 substantially as hereinbefore described with reference to Examples 1 and 2. rence to Example 3.

5 9. A process as claimed in claim 7 substantially as hereinbefore described with refe-

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